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# Morphology Study of Phosphonated Peptoid Block Copolymer

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Proton-conducting soft materials have attracted considerable attention since they play an important role as electrolyte membranes in both fuel cells and artificial photosynthesis.[1] The most widely studied electrolyte membranes are based on sulfonated polymers such as Nafion. However, sulfonic acid-based membranes are ineffective proton transporters at high temperatures (above 80 °C), since very little water is retained at high temperatures. Phosphonated polymers are attractive systems because they exhibit efficient proton transport under low water uptake conditions.[2] Herein we report the HAADF-STEM and Cryo-EM characterization of a sequence-defined phosphonated peptoid block copolymer (BCP): poly-*N*-(2-ethyl)hexylglycine-*block*-poly-*N*-phosphonomethylglycine (pNeh-*b*-pNpm). The structure of synthesized peptoid BCP is shown in Figure 1, and the synthesis details can be found elsewhere. [3]

In this work we studied the morphologies of BCP ultra thin films that had undergone various treatments in order to investigate the relationship between morphology and performance as electrolyte membrane. All thin films were produced by drop casting a 0.1 wt% MeOH/THF 50:50 solution on continuous carbon or lacey carbon films. Thin films were annealed in a humidity chamber using water vapor at 98% relative humidity and 25°C for 24 hours, followed by air drying. Hydrated samples were obtained by annealing the as-cast thin films in a Vitrobot at nominal settings of 100% humidity and 25°C and then plunging into liquid ethane after blotting. Self-assembled vesicles were prepared by dropping the solution into water. MeOH and THF were slowly evaporated subsequently at low vacuum. HAADF-STEM images in Figure 2 represent the morphologies of dry moisture-annealed thin films on continuous carbon supporting film (Figure 2a) and lacy carbon supporting film (Figure 2b) respectively. One can see honeycomb structures in Figure 2a with bright walls and bright center domains. The bright domains, which have higher atomic number, are the phosphorus-rich blocks in the peptoid. In contrast to the honeycomb structures on continuous carbon, Figure 2b reveals lamellar microphase separation after water vapor annealing. The lamellar structure with similar domain spacing are confirmed in bulk by small angle X-ray scattering as well, suggesting that the freestanding thin film on lacey carbon has the same microphase separated structure as bulk film. In contrast, the morphology of thin films on continuous carbon is significantly affected by interfacial energy so that it presents the honeycomb structure. The vitreous hydrated thin film on lacey carbon was then imaged by cryo-EM after annealing in order to illustrate the percolating network of conductive channels. The cryo-EM image in Figure 2c suggests a honeycomb structure with phosphorus-rich domains as walls and cores. The phosphorus-rich domains are responsible for the proton transportation when the film is hydrated. These conductive channels are much larger and uniform than the percolating networks in Nafion.[3] It is surprising to see that the hydrated freestanding thin film has morphology similar to the water annealed thin film on carbon substrate. This interesting phenomenon will be studied in future work. Figure 2d represents a

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